The Dielectric Properties of Thiacyclohexane

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The thermodynamic properties of thiacyclohexane were studied by J.P. McCullough and others[1] and it was shown that the entropy of fusion of this material is 2.002 e.u. at 292.25°K. They also found three phase transitions at 240.02°K, 207°K and 201.4°K. One of the present writers studied the structure of high crystalline modification of this material by means of X-rays[2]. According to his result, this high modification is in a disordered state in respect to the molecular orientation on the lattice site, and it was suggested that the high thiacyclohexane belongs to the category of the plastic crystals. This material shows a similar thermodynamic behavior and crystal structure with those of high cyclohexane, in spite of the fact that thiacyclohexane has the lower molecular symmetry, C_s, than that of cyclohexane, D_{3d}, and also has the permanent dipole moment of about 1.7 D. The investigation of the dielectric properties of this material will be interesting and may give more information than the study of non-polar compounds can provide, for the purpose of clarifying further details of the structure of high thiacyclohexane and of obtaining the informations of some properties of other phases. From this point of view the authors carried out the dielectric measurement of this material and found some interesting results on the rotational mechanism of the molecule in the crystalline phases of this material.

Experimentals

The electric circuit for the dielectric measurement is an audio-frequency transformer bridge described elsewhere[3]. The frequencies used for the measurement range from 100 to 3×10^4 c.p.s. The electric condenser for the measurement of the sample consists of platinum electrodes sealed in a soft glass cell in order to keep the sample between the electrodes under low pressure without exposure to air, as illustrated in Fig. 1. This cell can keep about 0.5 cc. of the sample and its electric capacity is about 0.2 p.f. in vacuum. It is enclosed in a copper block with the drying agent such as silica gel and is dipped in liquid air or in an oil bath. The dielectric constant

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[1] J.P. McCullough, et al., *J. Am. Chem. Soc.*, **76**, 261 (1954).

[2] S. Kondo, This Bulletin, **29**, 999 (1956).

[3] S. Kondo and T. Oda, ibid., **27**, 567 (1954).

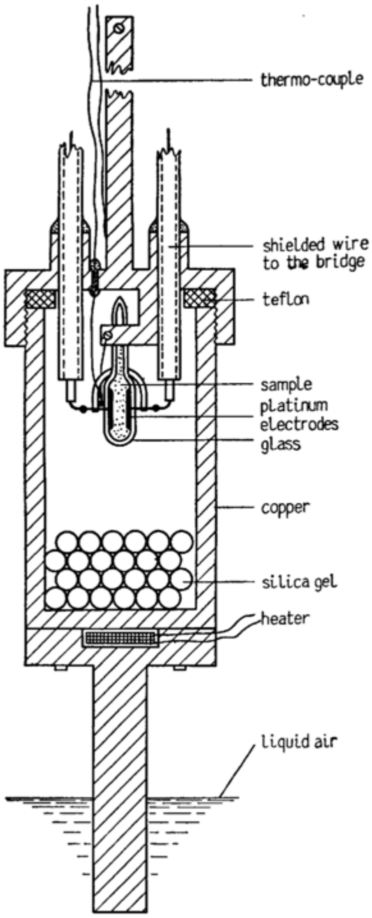

Fig. 1. The cell for the measurement of the dielectric constant of the sample.

of the sample can be determined by the comparison with those of purified benzene, carbon disulphide and ethyl ether. The sample was sent from the U.S. Bureau of Mines⁴⁾. The purity of the sample thus received was stated to be 99.99 per cent. This sample was sublimed and sealed in the cell in Fig. 1. All these procedures were carried out without exposure to air or day light. The liquid in the cell is cooled very slowly at the freezing point, in order to avoid the formation of voids or cracks during the solidification of the sample. The temperature of the sample can be maintained constant within ±0.1° for each set of observations with various frequencies. The dielectric constant of thiacyclohexane is shown in Fig. 2. There exist four condensed phases in this figure: liquid, solid phase III, solid phase II, and solid phase I according to the notation by McCullough and others1). The dielectric interpretations of this curve as well as of the dielectric loss data will be made in the following sections.

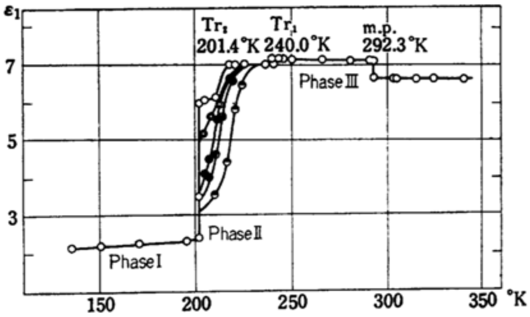

Fig. 2. The static dielectric constant of thiacyclohexane. The frequencies used for the measueement were 30 (◑), 10 (◉), 3 (●), 1 (◎), 0.1 (○) k.c.p.s.

Results and Discussion

Liquid and Solid Phase III.—The permanent electric dipole moment of thiacyclohexane in the liquid phase can be calculated by using the Onsager equation for pure polar liquid and is equal to 1.7 D. This value is equal to the dipole moment of this molecule estimated with the bond moment C—S, 1.4 D5), and the valence angle C—S—C, 105°1). No dispersion phenomena were observed in the liquid phase.

In the solid phase III which is considered to be plastic, the dielectric constant measured may not include experimental errors which may arise from voids or cracks since the melt is solidified so carefully that repeated solidifications show the same value of the solid dielectric constant and no cracks or voids were assured visually. The dipole moment of thiacyclohexane in the plastic phase can be calculated by using the Onsager equation6) and will give the same value as that in the liquid phase. This agreement seems to mean that the molecules in phase III behave in a manner roughly similar to those in the liquid phase except the fact that the molecules in the plastic phase are on the regular face-centered cubic lattice site. This dielectric interpretation is in good agreement with the result of thermodynamic1) and X-ray2) study of this material in the sense that these investigations revealed the very

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4) This sample of thiacyclohexane was provided by the American Petroleum Institute Research Project 48 on "the production, isolation and purification of sulfur compounds and measurement of their properties" and were prepared and purified at the Petroleum and Oil Shale Experiment Station, U. S. Bureau of Mines, Laramie, Wyoming, U.S.A.

5) G.C. Hampson, R.H. Farmer and L.E. Sutton, *Proc. Roy. Soc.* **A143** 147 (1933).

6) S. Kondo, *Memory of Osaka University of Liberal Arts and Education*, No. 6 (1957) (in press).

high disorder of molecular orientation in the phase III. In view of the existence of the relaxation phenomenon in phase II, there seems to be the molecular rotation with possibly smaller relaxation times and higher degree of rotational freedom, although in these two phases (the liquid phase and the phase III), there has been observed no relaxation phenomenon within the present frequency range. The value of dielectic loss, tan δ, is approximately equal to 3×10^{-4}.

Solid Phase II.—As seen in Fig. 2, The static dielectric constant of thiacyclohexane decreases by small amount from phase III to phase II at the transition point 240°K. The reason for this decrease could be either in the formation of many cracks during the phase transition which might decrease the apparent value of dielectric constant or in the intrinsic decrease of the dielectric constant in this phase II. Since no crystallographic or density data are available, it is impossible to decide which effect is more responsible for the decrease of the observed dielectric constant. However it may be supposed that the dipolar contribution still remains to some extent in this phase II, because the amout of change in the dielectric constant is comparatively small.

The low frequency dielectric dispersion was found in this phase. The Cole-Cole arcs are shown in Fig. 3 at 209.5° and 216°K. At a higher temperature, the high frequency side more than 30 k.c.p.s. was not measured and the Cole-Cole arcs were drawn by the extrapolation. The relaxation times τ were obtained from these arcs at various temperatures and these values range from 3×10^{-6} to 6×10^{-5} sec. The $\ln\tau$ vs. reciprocal temperature curve is shown in Fig. 4. The activation energy of this relaxation phenomenon is calculated from this curve to be 13.22 kcal. per mole and $\tau_0=5.75\times10^{-19}$ sec. This value of activation energy seems to be relatively greater than those which were found in such plastic crystals as *d*-camphor[7] and cyclohexane[8], determined by the dielectric and nuclear magnetic resonance experiments respectively, and which are considered to have the origin in the molecular rotations.

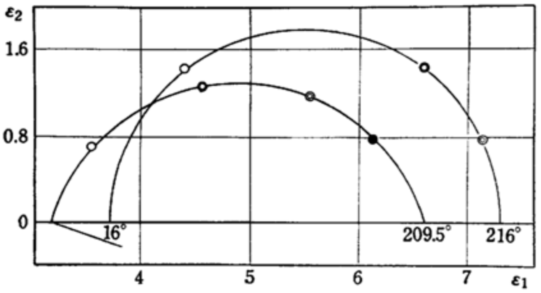

Fig. 3. The Cole-Cole plot of the dielectric relaxation of thiacyclohexane in the solid phase from 201.4°K to 200.02°K. The frequencies used are 30 (○), 10 (○), 3 (◎), and 1 (●) k.c.p.s.

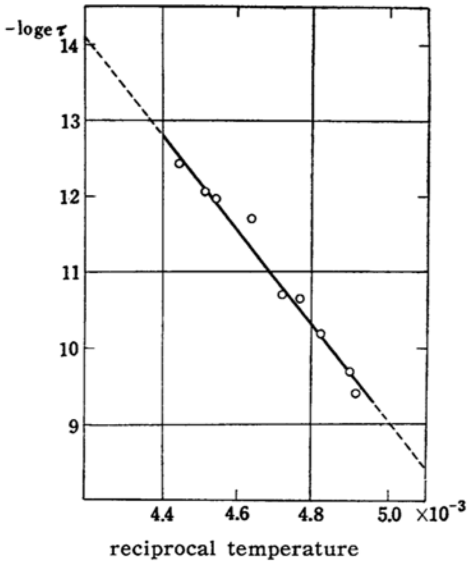

Fig. 4. The relaxation times vs. reciprocal temperature curve of thiacyclohexane.

The radii of the Cole-Cole arcs seem to increase at higher temperatures. The Onsager equation for pure polar liquid can be modified to the following expression for the mixed case such as one consisting of a rotator component and a non-rotator component of the same one molecular species[9]. That is,

$$N_1=\frac{9\boldsymbol{kT}}{4\pi\mu^2}\frac{(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty+2)^2},$$

where μ and N_1 are the dipole moment and the number of the rotating molecules per c.c. respectively, $\boldsymbol{k}$ is the Boltzman constant and T is the absolute temperature. If it is assumed that the thiacyclohexane molecules began to rotate with some degree of rotational freedom with the activation energy 13.22 kcal. per mole, whose diople moment was constant, and if the density of this solid phase II were constant in

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[7] J.G. Powles, *J. Chem. Phys.*, **20**, 148 (1952).

[8] E.R. Andrew and R.G. Eades, *Proc. Roy. Soc.*, **A216**, 398 (1953).

[9] Refer, for instance, H. Fröhlich, "Theory of Dielectrics", Oxford (1949), p 36.

this dispersion region, the increase of the Cole-Cole arc radii might mean the increase of N_1. Therefore one may think that the number of rotating molecules would increase by temperature elevation and thus there would appear the order-disorder state during the process of the increase of N_1. This dielectric interpretation seems to be in good agreement with the thermal study by McCullough and others[1]. They found the λ type heat anomaly which will be the transition of higher order. The crystal structure analysis of this phase will make these discussions clearer.

Phase I.—The dielectric constant drops to a very small value at the transition point 201.4°K by cooling. There is no dielectric dispersion in the present frequency range in this phase I. The value of the dielectric constant in this phase lies in the range of the square of the optical refractive index and thus there seems to exist only the contribution of atomic and electronic polarizability to the dielectric constant. In other words, there seems to be no dipole rotation or disorder of dipolar orientation of molecules on the lattice sites in this phase.

Summary

1) The molecules are in the rotational states in the solid phases II, III and liquid phase, and not in the phase I.

2) There is an order-disorder transition in phase II which may have its origin in the molecular dipole rotation.

3) The dielectric behavior in phase III is similar to that of other polar plastic crystals.

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